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A DISSERTATION SUBMITTED TO THE GRADUATE FACULTY IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

By

RONALD LYMAN McFARLAN

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THE EFFECT OF AN ELECTRIC FIELD ON THE X-RAY DIFFRACTION PATTERN OF A LIQUID

By Ronald L. McFarlan
Ryerson Physical Laboratory, University of Chicago

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Abstract

An investigation is made of the effect produced on the x-ray liquid diffraction pattern by an electric field so designed as to give the Kerr effect for the liquid under examination. The liquid diffraction pattern is obtained by replacing the crystal of a Bragg spectrometer with a cell containing the liquid. The electric field is approximately normal to the x-ray beam. Nitrobenzene is found to show an increase in peak intensity, on applying the field, ranging from four to seven times the probable error of observation, while benzene shows no observable effect. For the type of field used nitrobenzene shows a large Kerr effect, while benzene shows only a slight effect. Theoretical considerations indicate that this effect cannot be due to molecular orientation alone, but that an increase in the regularity of the spatial distribution of molecular scattering centers must occur.

Introduction

THE form of the x-ray liquid diffraction pattern is usually interpreted as being primarily due to the arrangement of the molecules in the liquid, the arrangement of the atoms in the molecule and the electrons in the atom producing secondary effects. To the space array of molecules producing this pattern one worker has given the name cybotaxis.[1] In attempting to derive a theoretical expression for the observed distribution of intensity in the liquid diffraction pattern Prins[2] assumes that;

1. The electricity (average electron density) is distributed continuously in each molecule.
2. This electricity vibrates in the plane of incidence of the x-ray wave.
3. The phases of the emitted partial waves from all the elementary volumes must be added in order to calculate the intensity of the diffracted ray for any particular angle of diffraction.

Starting with these assumptions Prins arrives at the following formula for the intensity of the scattered rays as a function of the angle of diffraction.

$$I(s) = N\overline{A}^2 + N\overline{A^2}\int_0^\infty dr 4\pi r^2 g(r)\frac{\sin sr}{sr} \qquad (1)$$

where $s = 4\pi/\lambda \sin \phi/2$, ϕ is the angle of diffraction, r represents the distance from a fixed but arbitrary center, and N is the number of molecules which scatter the x-rays. The scattering power A of a rigid molecule is thought of as localized at this center. The average of the scattering power over all possible

[1] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).
[2] J. A. Prins, Zeits. f. Physik **56**, 617 (1929).

orientations of the molecule is indicated by the horizontal line above A. The function $g(r)$, first introduced by Zernicke and Prins,[3] describes the distribution of molecular scattering centers throughout the liquid, and is defined in such a way as to make $4\pi r^2 dr\, g(r)$ represent the probability that a molecular center will lie between a distance r and $r+dr$ from a fixed but arbitrary center. The first term on the right-hand side of Eq. (1) gives the intensity due to N molecules scattering independently. The second term takes account of the interference between the rays scattered by the different molecules, and may have a negative sign.

It is a well-known phenomenon of optics that if certain liquids are placed in a strong electric field they become slightly double-refracting, behaving somewhat like a uniaxial crystal. This experiment was originally performed by J. Kerr,[4] and is known as the Kerr effect. It has, perhaps, been most successfully explained by the orientation hypothesis as developed, by Langevin Born, and others.[5] According to this hypothesis when an electric field is applied across a liquid an asymmetry is produced in it as a result of a tendency of the molecules to orient themselves in a definite direction with respect to the field because of the electric moment associated with each molecule. Two factors may contribute to the presence of this moment. In the first place the molecule may not be equally polarizable in all directions, and consequently will endeavor to set itself so that its axis of maximum polarizability is turned parallel to the field. Secondly, there may be a permanent moment associated with the molecule. Both factors are usually present.

Now, if an electric field applied across a liquid produces in the molecules a tendency to orient themselves in a particular direction with respect to the field, and consequently produces an asymmetry in the liquid it might be expected that the angular distribution of the intensity of the scattered x-rays would be altered. Since the liquid diffraction pattern is primarily molecular in origin there are two possibilities to be considered. The first is the effect which the electric field would have on the scattering of the molecules considered separately, while the second is the effect on the distribution of molecular scattering centers throughout the liquid.

Calculation of the Anticipated Effect

The effect of the field on the molecules scattering separately can be considered in the following manner. Assume that the molecules are diatomic, that they have a permanent moment m, and that the scattering power of each atom is located at its center. Then, referring to Fig. 1, the scattered intensity due to the electric vector of the incident beam which is parallel to the plane XOP will be[6]

$$I_{11} = 4\beta A_\phi^2 \cos^2\left(\frac{4\pi a}{\lambda} \sin\frac{\phi}{2} \cos\alpha\right) = 4\beta A_\phi^2 \cos^2(x \sin\alpha)$$

[3] Zernicke and Prins, Zeits. f. Physik **41**, 184 (1927).
[4] J. Kerr, Phil. Mag. **50**, 337 (1875).
[5] Cf. P. Debye, Marx Handbuch der Radiologie, Vol. VI, p. 754
[6] A. H. Compton, X-rays and Electrons, Appendix IV, p. 384.

where $2a$ represents the distance between the atomic centers, $A_\phi = zAe^2\cos\phi/rmc^2$, z represents the number of scattering electrons in each atom, ϕ is the angle of diffraction, β is a constant defined by $I = \beta A^2$ and $x = 4\pi a/\lambda \sin \phi/2$.

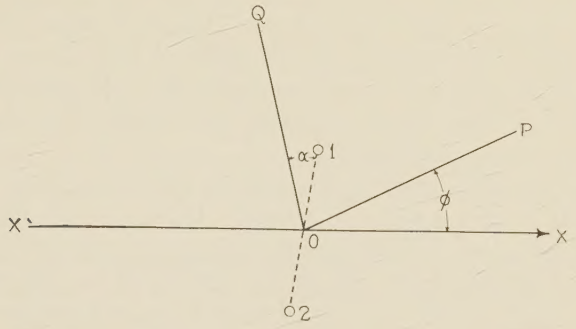


Fig. 1.

If an electric field of strength E is applied in the direction OQ the probability that the moment m will lie in a solid angle $d\Omega = \sin \alpha d\alpha d\psi$ is, according to the Boltzmann-Maxwell law

$$\frac{1}{4\pi} e^{mE\cos\alpha/kT} \sin \alpha d\alpha d\psi .$$

The average intensity of I_{11} that is scattered in the direction ϕ on applying the field E is then

$$I_{11} = \frac{4\beta A_\phi^2}{4\pi} \int_{\psi=0}^{\psi=2\pi} \int_{\alpha=0}^{\alpha=\pi} \cos^2 (x \cos \alpha) e^{mE\cos\alpha/kT} \sin \alpha d\alpha d\psi$$

$$= 2\beta A_\phi^2 \left[P(x) + \frac{m^2E^2}{2k^2T^2} Q(x) \right]$$

where

$$P(x) = 1 + \frac{\sin 2x}{2x}, \quad Q(x) = \frac{1}{6} + \frac{\sin 2x}{2x}\left[1 + \frac{1}{4x^2}\right] - \frac{\cos 2x}{2x^2},$$

and powers of mE/kT greater than the second are neglected. Following the usual method the total intensity of the scattering at an angle ϕ is found to be

$$I_\phi = 2ZI_e \left[P(x) + \frac{m^2E^2}{2k^2T^2} Q(k) \right] \tag{2}$$

where I_e is the scattering at an angle ϕ due to a single electron. It will be seen that the effect should be proportional to the square of the field applied. A similar calculation was carried out for a model of the nitrobenzene molecule in which five CH groups and one NO_2 group were evenly spaced on the circumference of a ring. It was assumed that these groups scattered as units, and that the ring possessed a permanent moment due to the asymmetry produced by the NO_2 group. An intensity formula analogous to Eq. (2) was obtained and as in Eq. (2) $P(x)$ and $Q(x)$ were found to be of approximately

the same order of magnitude. In order to estimate the relative importance of the additional term introduced because of the presence of the electric field let E be taken as 5 k.v. per cm, one of the values used in this experiment, let m be given the value 3.9×10^{-18} e.s.u. as determined by polarization measurements,[7] let T be taken as 300°K, and k given its usual value 1.39×10^{-16}. The value of $m^2E^2/2kT^2$ then becomes of the order of 10^{-6}. It would thus seem that the effect of the field on the scattering of the molecules considered independently would be very small, probably too small to be detected by the usual methods of measuring intensity.

On the other hand the optical effect of the electric field on the liquid is to make it act as if it were a uniaxial crystal. If the electric field tends to arrange the molecules into something approximating crystalline structure the second term on the right-hand side of Eq. (2) would be affected, in that the distribution function would correspond to an increased regularity in the spatial arrangement of the scattering centers. The effect on the diffraction pattern would be an increase in the intensity of the peak, and also a sharper peak. Thus in looking for an effect of the electric field on the liquid diffraction pattern it would appear best to investigate the peak intensity with and without the field. This has been done in the following experiment.

Experimental Procedure

The cell in which the liquids were put for investigation is shown in Fig. 2. The window was made of cellophane 0.025 mm thick, on the inner side of

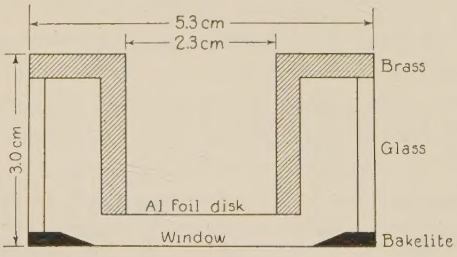


Fig. 2. Diagram of cell.

which aluminum leaf 0.00065 mm thick was fastened. The high potential was applied to the aluminum leaf by means of the electrode E, Fig. 3, and a strip of aluminum foil leading from the electrode to the inner side of the window. Separated from the window by a distance of 3.5 mm was a heavy aluminum foil disk which was grounded by means of the earthed brass back of the cell. The x-rays entering through the window were scattered by the liquid lying between the window and the aluminum foil disk. In this way the field was given the direction OQ of Fig. 1 with respect to the x-ray beam. Fig. 3 illustrates the arrangement of the apparatus used.

In order to apply the field as nearly at right angles to the x-ray beam as possible, since the Kerr effect is observed when the light beam is traveling

[7] P. Debye, Polar Molecules, p. 54.

normal to the field, the ordinary Bragg crystal reflection method was used to obtain the x-ray diffraction pattern. The incident x-ray beam was collimated by a Soller slit set each slit of which was 9 cm long, 1.5 cm high, and 0.045 cm wide. Attached to the front of the ionization chamber and rotating with it was another slit set with slits 6 cm long, 1.5 cm high, and 0.022 cm wide. An adjustable slit, kept at a width of about one mm, was placed between the second slit set and the celluloid window of the ionization chamber. This slit system served to prevent the rays scattered either by the cellophane-aluminum window, or the aluminum disk at the back of the cell from entering the ionization chamber. The chamber was filled with methyl bromide at atmospheric pressure, and the ionization currents were measured by a Compton electrometer adjusted to a sensitivity of 10,000 mm divisions per volt at a scale distance of 3 meters. Unfiltered x-rays obtained from a molybdenum-target tube operated at 35 k.v. and 32 milliamperes were used. The current supplied to the x-ray tube was rectified by means of a full-wave balanced-circuit kenotron rectifier.

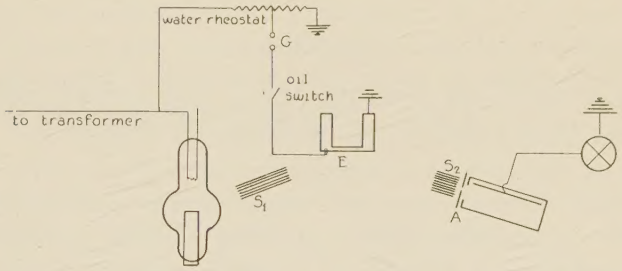


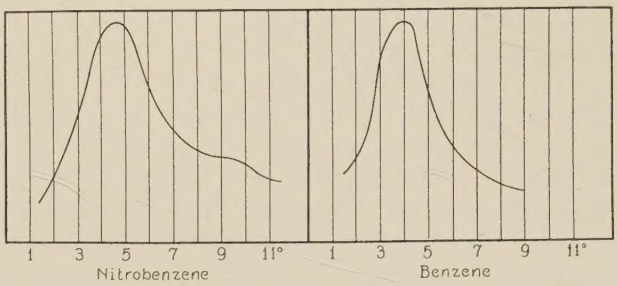
Fig. 3. Arrangement of apparatus.

Since the Kerr effect is most prominent when the electric field consists of a rapid succession of short, sharp peaks it was thought best to look for the effect with the same type of field. In order to synchronize the peaks of the applied field with the peaks of the voltage across the x-ray tube the same high voltage source was used for both. The voltage applied to the cell was stepped down by means of a water rheostat. The peaks of the electric impulses across the cell were sharpened by means of a spark gap, across which a jet of air was blown, inserted between the rheostat and the cell. This device permitted the use of higher fields, and also gave a field more nearly like that used in observing the Kerr effect for nitrobenzene.

With this arrangement the liquid diffraction curves shown in Fig. 4 and Fig. 5 were obtained. These curves do not differ appreciably from the diffraction curves obtained by other methods. They show the same approach toward zero scattering at small angles of diffraction, and the same principal maximum of intensity. The nitrobenzene curve appears to be somewhat broader than the benzene curve.

To observe the effect of the electric field on the diffraction pattern the cell and ionization chamber were set at angles corresponding to the diffraction

peak. The following procedure was observed in taking all readings. The field was applied across the cell, and 45 sec. later an observation of the intensity was made. The field was then removed, and 45 sec. were allowed to



Figs. 4 and 5. Diffraction curves.

elapse before the reading without the field was taken. Alternate readings, with and without the field, were taken in this way for nitrobenzene and benzene.

Results

The results obtained are shown in Table I. The + sign is used to indicate an increase in peak intensity on applying the field, the − sign a decrease. The probable error listed in each case is the probable error of the arithmetic mean as computed in the ordinary way from least squares theory. The values given for nitrobenzene under fields of 5 k.v. per cm and 9 k.v. per cm, and for benzene represent the average of 100 pairs of readings taken as described above. The change in intensity listed for nitrobenzene under a field of 14 k.v. per cm is the average of 37 pairs of readings, the breaking down of the cell preventing further observations at this voltage. With so strong a field it was difficult to obtain steady conditions, and the results are not as reliable as the others listed.

Table I.

Liquid	Field Applied	Intensity Change	Probable Error
Nitrobenzene	5 kv per cm	+0.8 percent	0.2 percent
Nitrobenzene	9 kv per cm	+2.3 percent	0.3 percent
Nitrobenzene	14 kv per cm	+2.0 percent	0.8 percent
Benzene	9 kv per cm	−0.3 percent	0.3 percent

The same type of field was used for all observations. With this type of field benzene shows only a slight Kerr effect. As is seen the change in peak intensity for benzene is not significant, and is in the direction of lesser instead of greater intensity. This lack of any definite shift for benzene rules out the possibility that the effect observed for nitrobenzene might be due to mechanical causes such as the bending of the cellophane window as a result of electrostatic forces of attraction.

The increase in peak intensity for nitrobenzene appears to be a function of the potential drop across the cell. On the basis of the observations made for the two lower voltages it might appear as if the effect varied approximately as the square of the potential applied. Further experiment is necessary, however, to decide this point definitely. But it is reasonably certain that over a range of field strengths less than 9 k.v. per cm the effect increases with increasing field strength. The observations made at 14 k.v. per cm are not sufficiently accurate to permit any definite conclusions to be drawn from them.

Conclusions

Since the observed changes in intensity range from four to seven times the probable error, and as mechanical effects do not produce them it seems reasonably certain that the type of electric field described above produces an increase in the peak intensity of the nitrobenzene diffraction pattern. This change is a function of the strength of the field applied, and from the data now available appears to vary as the square of the field strength over a range of potential gradients less than 9 k.v. per cm.

The effect is far larger than would be expected from the orientation of the molecules considered as scattering separately. It would thus appear that molecular orientation alone is not capable of producing the observed change. If, however, the effect of the field is to bring about a more orderly arrangement of the molecular scattering centers with an increased regularity in the spatial distribution of these centers then such an effect as that observed might be expected. Such a tendency toward a crystalline arrangement was the explanation originally advanced by Kerr to account for the effect he observed.

It is possible that the effect just described is not associated with the Kerr effect, and that the correlation obtained for nitrobenzene and benzene is due to the large difference in their permanent moments. Liquids are known with permanent moments of the same order of magnitude as nitrobenzene but which do not show a Kerr effect of the same order of magnitude. Experiments with some of these liquids are desirable in order to gain further information regarding this point.

In conclusion the author wishes to express his appreciation to Professor A. H. Compton for his very helpful advice and his constant interest in the problem.